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THE ELASTOMER RESEARCH and DEVELOPMENT PROGRAM of the

DEPARTMENT OF THE ARMY

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ANNUAL REPORT

MARCH 1961

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QUARTERMASTER RESEARCH & ENGINEERING COMMAND

NATICK, MASSACHUSETTS

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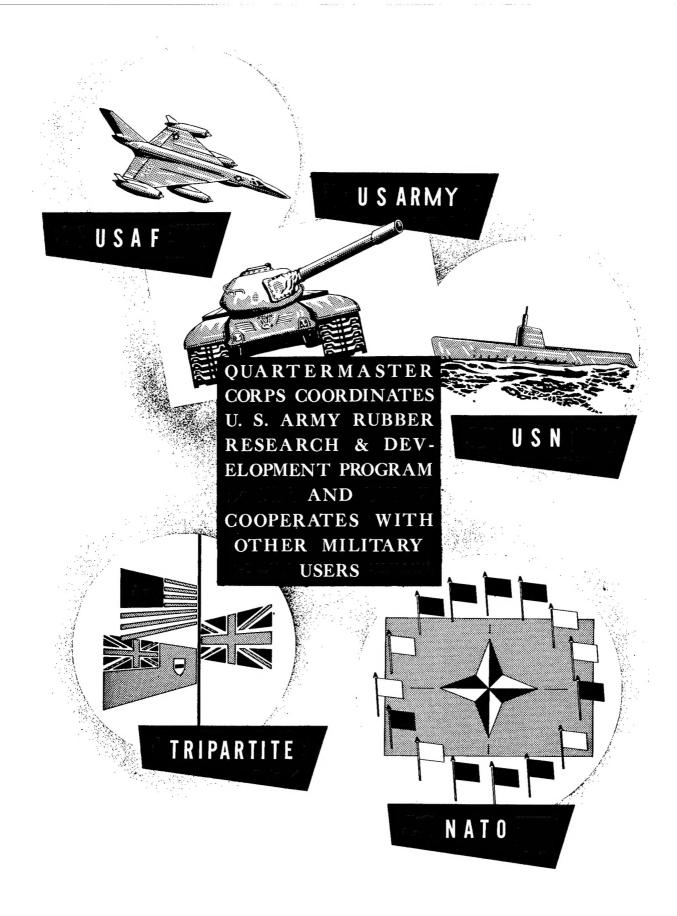
# THE ELASTOMER RESEARCH AND DEVELOPMENT PROGRAM OF THE

DEPARTMENT OF THE ARMY

ANNUAL REPORT

MARCH 1961

Quartermaster Research and Engineering Command Natick, Massachusetts



#### FOREWORD

This report was prepared by the U. S. Army Quartermaster Corps under the authority and responsibilities contained in Department of the Army Research and Development Directive No. 24, dated 2 June 1960. The Quartermaster General was originally assigned responsibilities for "primary cognizance for research applicable to the development of elastomers and other rubber-like materials for use in any geographical area, and for exchange of pertinent information" by Secretary of the Army Memorandum CSGLD/F1 9748, dated 10 March 1949.

Significant accomplishments made in the Department of the Army Elastomer Research and Development Program during the period March 1960 to March 1961 by the Chemical Corps, Corps of Engineers, Medical Service, Ordnance Corps, Quartermaster Corps, and Signal Corps are contained in this Annual Report. Also presented are projected plans for scientific research directed toward fulfilling difficult and unresolved rubber requirements needed to support future military operations.

Recognizing the continuing need for improved elastomers by all Military Services, and also our Allies, the Quartermaster Corps has maintained cooperative efforts in this Program on inter-Departmental, National, and International levels. International exchange of information is being maintained with our counterparts in England and Canada through Tripartite, and with other countried through NATO, and the International Standardization Organization, Technical Committee on Rubber (ISO/TC45).

All contributions to this Program, and cooperation in supplying information for this report, are gratefully acknowledged.

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#### SUMMARY

The Department of the Army Elastomer Research and Development Program covers a comprehensive investigation in the field of rubber chemistry and technology, including (a) research in the synthesis of monomers, many of which are new, (b) development of polymerization methods to convert these monomers into elastomers, (c) exploratory research studies on vulcanization, particularly those new rubbers which do not respond to conventional and development so that these rubbers may be used to maximum advantage in the fabrication of military equipment and components. Steady progress and significant advances have been made during the past year, including:

1. Synthesis of a family of nitroso rubbers. In addition to the copolymer of trifluoronitrosomethane (CF $_3$ NO) and tetrafluoroethylene (CF $_2$ =CF $_2$ ) reported last year, a family of experimental nitroso rubbers has been synthesized. Current research on nitroso derivatives is very promising. The following monomers have been copolymerized with CF $_2$ =CF $_2$  to produce nonflammable elastomers:

NO2CF2CF2NO, ClCF2CF2NO, CF3CF2CF2NO and HCF2CF2NO.

- 2. Improved vulcanization of copolymer of CF<sub>3</sub>NO/CF<sub>2</sub>=CF<sub>2</sub>. Last year this rubber was reported to possess unusual chemical resistance, good flexibility at low temperatures and nonflammability. During this report period, a vulcanizing system was developed for this rubber, using a combination of amines and carbamates as crosslinking agents. Tensile strength of the vulcanizates were increased from 200 p.s.i. to 700 p.s.i. Compounding investigations will be continued in an effort to further increase tensile strength and develop coating formulations for fabrics to fully exploit the non-flammable characteristics of this rubber for thermal protective devices and other applications.
- 3. Synthesis of an experimental silicate elastomer. A flexible and elastic silicate polymer has been prepared by the reaction of sodium hydrogen silicate and dimethyldichlorosilane. This polymer was cured by exposure to gamma radiation from a Cobalt-60 source, resulting in a rubbery product. It retains its flexibility in temperatures as low as minus 80°C. Its continued exposure to temperatures over 100°C. resulted in loss of water, hardening, and embrittlement. Nevertheless, results obtained thus far look very promising. It has been reported that the polymer is stable for short periods at temperatures as high as 650°C. This investigation will be extended to include various types of silicates.

- 4. Development of an effective antirad (1,1%-diphenyl-2-picryl-hydrazine) for nitrile rubber. This antirad seems to be specific to nitrile rubber inasmuch as it does not afford any radiation protection to natural rubber.
- 5. Development of a polyurethane compound for track pads of tanks. A polyurethane compound has been developed; it showed significant improvement over the standard items. Road testing of the track pads at Aberdeen Proving Ground (highest ambient temperature of test was 80°F.) was performed over 2,000 miles of gravel, paved, and unimproved roads. During operation, the polyure—thane pads remained an average of 25°F. cooler than standard pads made of sty—rene-butadiene rubber. In addition to uniform wearability, minimum chunking and chipping, the polyurethane pads provide much longer service life than the standard SBR pads. Track pads have been made from the best polyurethane compound developed thus far and will be road tested at Yuma, Arizona, where ambient temperatures are as high as 125°F.
- 6. Development of dipped unsupported butyl-rubber glove. A satisfactory dipped, unsupported butyl-rubber glove has been developed. It is currently being type-classified for standard use in handling Chemical, Biological, and Radiological (CBR) Agents. Producing dipped articles from butyl rubber has been attempted for many years because of its excellent inherent impermeability to these dangerous agents. The difficulty has been in eliminating trapped air bubbles in the finished product. This was successfully solved by developing the proper butyl rubber compound, and by improving the dipping techniques. The dipped gloves are less expensive than molded gloves, and there is no sacrifice in serviceability.

# THE ELASTOMER RESEARCH AND DEVELOPMENT PROGRAM

OF THE

#### DEPARTMENT OF THE ARMY

#### I. INTRODUCTION

Research and development in the field of rubber is of vital importance to the success of military operations. Rubber is a component of innumerable Army items, such as tires for military vehicles, hoses and containers for gasoline, fabric coatings for uniforms, gaskets and seals for hydraulic systems, and binders for solid propellants in rockets and missiles.

Before World War II, military rubber requirements were relatively simple. Today, global operations demand that rubbers maintain their functionality at extremely low temperatures (-78°F. recorded in Greenland). The problem would be less difficult if a rubber with one specific property would suffice. For example, a rubber is available that is flexible at -80°F., but is not resistant to fuels. This rubber, therefore, cannot be used for fuel hoses in Arctic operations. On the other hand, there are also rubbers that are resistant to fuels but become stiff and inflexible at subzero temperatures. Tremendous changes in the development of new weapons systems have created additional and more difficult rubber problems. Rubbers which resist the deteriorative effects of concentrated acids and strong oxidizers are needed for the protection of personnel who handle propellants and potent chemicals for rockets and guided missiles. Rubbers which can minimize the deleterious effects of flame and thermal radiation are also needed for the fabrication of protective items and equipage that may be exposed to nuclear blasts. Concentrated efforts, therefore, must be directed toward developing new rubbers that possess a combination of several of the desired chemical and physical properties.

#### II. MAJOR OBJECTIVES

The overall activities of the Department of the Army Elastomer Research and Development Program can be categorized into the following principal objectives:

- a. Research directed toward developing new elastomers possessing a combination of the following characteristics:
  - 1. Flexibility at low temperatures (-40°F., and lower).
  - 2. Resistance to the deteriorative effects of chemicals and potent oxidizers such as concentrated acids, aromatic hydrocarbons and other types of propellants.
  - 3. Stability at high temperatures (600°F., and higher).
  - 4. Resistance to flame, or nonflammability.
  - 5. Resistance to ionizing radiation.
  - 6. Resistance to ozone and weather.
  - b. Vulcanization and screening evaluation of newly-developed elastomers.
- c. Compounding development on various types of elastomers, both experimentally and commercially available, to produce materials that can be used to fabricate military items.

#### III. ACTIVITIES OF THE TECHNICAL SERVICES

# 1. CHEMICAL CORPS

The Chemical Research and Development Laboratories and the Engineering Command, Army Chemical Center, Maryland, undertake rubber research and development to meet the needs of the Chemical Corps. Their continuing interests on rubber applications are for protective masks, thickeners for incendiaries and toxic agents, and coatings for protective clothing used for handling strong oxidizers and chemical agents.

Compounding for Protective Masks. The tendency in the past has been to produce protective masks from nonblack natural rubber compounds. Consequently, much of the compounding and production "know-how" was based on formulations with mineral pigment reinforcement. Under a cooperative project with General Tire and Rubber Company, a systematic compounding study, using carbon black reinforcement for protective masks, has been undertaken by the Chemical Corps. The overall objective is to develop masks which are more durable, ozone and tear resistant, nontoxic to the skin, low modulus, and flexible at extremely low temperatures. For durability, the use of various types of carbon blacks showed that 30 parts of Super Abrasion Furnace (SAF) black and 10 parts of plasticizer (based on 100 parts of natural rubber) in a rubber compound, impart outstanding tear resistance and a tensile strength of about 4,000 p.s.i. The compound also has good puncture resistance. Accelerator study showed that 1.0 part of Santocure, in combination with 1.5 parts of sulfur, is suitable. As a plasticizer, dioctyl phthalate gave the best results. There were several limitations on compounding for ozone resistance due to toxic effects on the skin. Tests show that 4 parts of Flectol H and 2 parts of wax give a good combination for ozone resistance and, at the same time, meet the requirements of toxic effects.

In addition to natural rubber, some work has been done on other polymers. One would expect cis-polyisoprene to have properties like natural rubber. However, the limited work with this material showed that direct replacement of the natural rubber in the same formulation does not give an equivalent compound. The tensile strength, although satisfactory, is somewhat lower. Obviously, much more compounding work has to be done to adapt cis-polyisoprene for use in protective masks. The use of silicone rubber is another interesting possibility.

Materials Research. Under Project 4C-93-30-001, the objective is the development of polymeric materials, resistant to various chemical warfare agents and environmental conditions. Where possible, the preparations of new compounds should be elucidated by fundamental studies of the organic and physical chemistry of the systems involved. The program has yielded a variety of compounds which in actual test successfully withstand continuous (16 days) exposure to both GB and VX warfare agents. It was also found that isotactic modifications of conventional and nonconventional polymers show unusual resistance to simulated chemical agents (dioctyl hydrogen phosphite) and to actual chemical agents (GB and VX). Polystyrene, which is an economically attractive material in its amorphous form, is notoriously poor in its performance as evidenced by quick dissolution; but, when made in isotactic variations, no apparent attack was observed. Attempts are being made to correlate other aspects of polymer structure to their resistance to toxic chemical agents. These aspects include effects of crystallinity, melting point, molecular weight and chemical structure of the polymers. In addition to polystyrene, other materials under investigation are polypropylene, polyethylene, polyvinyl chloride, and substituted polystyrenes. Results, thus far obtained, show that crystallinity and isotacticity play an important role in designing new polymeric systems for improving chemical resistance.

Other Projects. The Chemical Corps, in cooperation with the Quartermaster Corps, has been working on improved components for protective clothing. This work includes unsupported gloves as part of the protective clothing ensemble used in handling CBR agents. A satisfactory dipped unsupported butyl rubber glove has been developed which is now currently being type-classified for standardization.

Investigations are also in progress on the use of elastomeric materials as fuel thickeners for incendiary bomb fillings. Another phase is on thickened toxic agents for spray applications. For this purpose, dilute solutions of various low molecular weight polymers are being investigated.

#### 2. CORPS OF ENGINEERS

The Elastomer Program of the Corps of Engineers is administered by the Engineer Research and Development Laboratories, Fort Belvoir, Virginia.

Exposure studies initiated last year on 14 styrene-butadiene rubber compounds were continued at various test sites, including Fort Churchill, Can.; Yuma, Ariz.; and Ft. Belvoir, Va. This work was directed toward developing ozone-resistant vulcanizates for cable and wire applications. Results agreed essentially with related accelerated laboratory ozonator tests. After a 24-month exposure of compounds in Yuma, Arizona, the compound containing 3 parts (per hundred parts of rubber) of N,N:-dimethyl-N,N:-di-(methyl propyl) p-phen-ylenediamine (Eastozone 32) was practically unaffected, and showed no loss in tensile strength. In contrast, the control sample containing no antiozonant lost 60 percent of its original tensile strength after three months, and 90 percent after six months. The second best compound contained a combination of two antiozonants (UOP88 and Santoflex AW), which had lost 25 percent of its original tensile strength after a 24-month exposure. The best compounds obtained will be investigated for fabric coating applications.

Efforts were directed toward developing polyester elastomers possessing low-temperature flexibility and solvent resistance. The monomers were selected from diacids, diacylhalides, diols, and triols. The polymers were prepared by condensation polymerization and were chain-extended and cross-linked with discovanates. Due consideration was given to the desired spacing of the ester, nitrogen, and urethane groups of the polymer chain in such a manner as to give maximum disruption of orderly array of units along the molecular chain. Based upon past experiences, consideration was also given to the distances between linkages along the chain, substituents on the nitrogen atoms, and crosslinking sites inasmuch as these factors affect rubbery properties, solvent resistance, and crystallinity of the resulting polymer.

The polymer that possessed the best combination of physical properties, afforded resistance to attack by aliphatic hydrocarbons, and retained flexibility at low temperatures, was prepared by (1) condensation reaction of methyl diethanolamine with a mixture of C10 diacids and triethanolamine and (2) chain-extending and cross-linking the resulting terpolymer with hexamethylene diisocyanate. However, the rubbery material obtained was not very stable because it deteriorated gradually when stored in the open under normal room temperatures. The polymer was very susceptible to hydrolysis, even from the moisture present in the air. During the first month of shelfstorage, there was no noticeable change; in two months it had become softer; and after three months, it became tacky and semiliquid on the surface. The vulcanizate of this rubber (using hexamethylene diisocyanate as vulcanizer and carbon black as reinforcement) gave a tensile strength of only 200 pounds per square inch, and 250 percent ultimate elongation. Further research is needed to improve this rubber, particularly in its resistance to atmospheric depolymerization.

# 3. MEDICAL SERVICE

Elastomeric materials research for medical applications is conducted by the Army Prosthetics Research Laboratory, Army Medical Center, Forest Glen, Maryland.

The primary interest of the Medical Service in elastomers is the use of these materials in the preparation of internal and external prostheses. Further improvements were made last year in the fabrication of foamed acrylate terpolymer and crimped Dacron composite tubes for vascular grafts. They have been produced in sizes with inside diameters ranging from 3 mm. to 32 mm. for both animal and clinical use. Production reports continue to be favorable.

Modifications have been made in the monomer ratios and compounding techniques of the terpolymer to produce synthetic elastomer latices for other medical and surgical uses. One of these shows real promise as a substitute for cartilage. This material has undergone rigorous laboratory testing under conditions simulating those of ambulation. If laboratory tests on animals prove fruitful, this "cartilaginous" acrylate could be useful in the treatment of severe arthritis.

The standard terpolymer is being used experimentally as bile ducts, ure ters, and esophagae. Its use as tracheae has already been demonstrated.

This foam material is being used in conjunction with silicone rubber for tissue ingrowth and thereby provides anchorage and stabilization for heart valves.

Tendon sheaths have also been prepared from this material. Commercial production of the base latex has been successfully achieved. Current laboratory development has resulted in a latex having up to 50 percent solids in contrast to the usual 36 percent, or 37 percent of regular production.

A soft stump socket for leg amputees consisting of the regular terpolymer, faced or coated with a copolymer of butyl acrylate—acrylonitrile, is an example of a new application for external prostheses. Another application has been that of a soft denture line for false teeth.

Improvements are continuing to be made in other areas of external prostheses, such as cosmetic gloves, facial prostheses, and leg covers. Specific examples of internal prostheses are shown in figure 1.

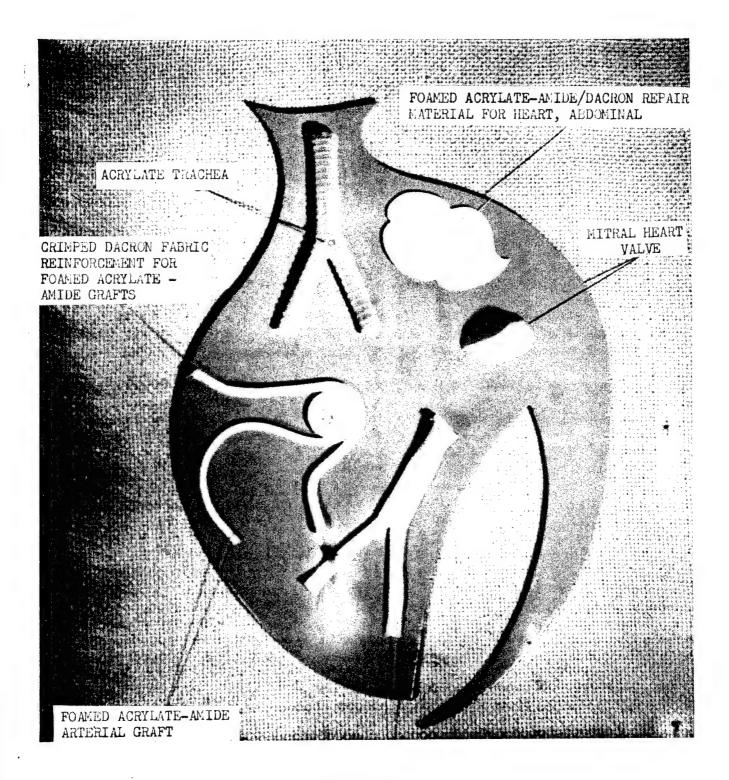


Figure 1

Improved elastomers provide material for use in internal body prostheses, such as grafting or replacing arteries, tracheae, and heart valves.

# 4. ORDNANCE CORPS

Ordnance Corps activities on rubber research and development are carried out in various arsenals. The administration of the research phase is under the Ordnance Materials Research Office (OMRO) at Watertown, Massachusetts. The major portion of the laboratory phase is concentrated at the Rock Island, Illinois, and Detroit, Michigan arsenals.

Rock Island Arsenal. The Rubber Laboratory at Rock Island Arsenal monitors most of the elastomer research of the Ordnance Corps, although funding is directed by OMRO, Watertown Arsenal. One of the major concerns of Rock Island is the need for radiation and/or heat-resistant elastomers.

Synthesis of Radiation and/or Heat Resistant Elastomers. The limitations of currently available elastomers with respect to thermal stability and resistance to the damaging effects of high energy radiation are well recognized. To keep pace with advanced weapons and support for future developments, it is essential that new elastomers or elastomeric compositions be developed which provide improved heat and radiation resistance. With this objective in mind, a program has been initiated at Rock Island Arsenal for extending the useful service life of both general purpose and specialty elastomers, when they are subjected to thermal and radiation environments.

Rubbery products of moderate molecular weight (up to 20,000) have been prepared using the following general condensation reaction:

clco-R-cocl + Ho-R<sub>1</sub>-OH cl(cor-coor<sub>1</sub>-O)<sub>n</sub> H where R may be aliphatic and R<sub>1</sub> aromatic, or where R is aromatic and R<sub>1</sub> aliphatic. The reaction product of 4,4:-isopropylidene bis(2-isopropylphenol) and sebacoyl chloride has been of special interest. Preliminary attempts to vulcanize this polymer with peroxides, amines, carbamates, and diisocyanates have been unsuccessful. A partial cure was obtained with tolylene-2,4-diisocyanate. Future efforts will consist of introducing functional groups in a polymer that will provide thermally—stable vulcanization sites.

A phase of this program covers arylene-modified silicone elastomers. In view of the excellent thermal-oxidative stability of available silicone rubbers and their property retention over a broad temperature range, it was believed that appropriate structural modifications within this class of rubbers would lead to the desired objectives. The incorporation of arylene units into the main chain of the siloxanes appeared to be especially appealing since the resonance stabilization in such systems would be expected to contribute to both thermal and radiation stability. Three arylene-modified siloxanes have been synthesized. They were cured with distert-butyl peroxide and reinforced with silicon oxide (Cab-O-Sil), but evaluation revealed that the arylene-modified siloxanes are no better than commercially available silicones in their thermal-oxidative stability.

The second phase of this program covers the synthesis of fluorinated arylene-modified siloxanes by the incorporation of fluoromethylene groups. The perfluoromethylene groups are known to have excellent thermal stability and it was considered that they would provide a sufficient degree of flexibility to produce elastic characteristics to the polymer. At present, the preparation of the silane monomer has been accomplished with low yields, but polymerization was not successful.

A third phase of the arylene-modified siloxanes is the silcarbanes in which oxygen replaces the perfluoromethylene groups between the two arylene structures. An oil has been obtained from the condensation of  $\mu_{\mathfrak{p}}$  dilithiodiphenyl ether and dimethyldichlorosilane and silicon-containing solids from the Wurtz condensation of dibromodiphenyl ether and dimethyl-dichlorosilane.

A program has been initiated for developing elastomers and resins that are stable at high temperatures. Attempts have been made to synthesize polymers from asbestos, silica compounds, phosphates, borates, mica, meta silicates, orthosilicates and dialkyldichlorosilanes, such as dimethyl and diphenyl dichlorosilanes. A flexible and elastic silicate rubber has been prepared by the reaction of sodium hydrogen silicate and dimethyldichlorosilane. This polymer was cured by exposure to gamma radiation from Cobalt-60 source, resulting in a rubbery product. It is flexible at temperatures down to minus 80°C.; however, continued exposure at temperatures over 100°C. results in loss of water, hardening, and embrittlement. It is reported to be stable for short periods at temperatures up to 650°C. This investigation will be extended to include various types of silicates such as the dipart and tri-silicates, and various alkyl and aryl halosilanes.

Investigations are also in progress to develop heat-resistant materials for use as rocket motor liners. One approach is on semi-inorganic and the other is on organic materials. Experimental work on the semi-inorganic approach covers these phases: (1) curing studies using commercial silicones with organometallic hydrides, (2) development of experimental techniques for synthesizing specialty silicone gums, and (3) synthesis of several elastomeric stannosiloxane copolymers having Si: Sn ratios of 3:1 to 6:1 and molecular weights ranging from 3200 to 9700. It also includes synthesis of siloxane containing aluminum atoms in the main chain. Curing studies will be carried out on promising elastomers in these classes.

The main objective in the organic approach to this problem is the internal plasticization by chemical modification of the polymer structure and/or by external plasticization with rubber, of those plastic resins, known as excellent thermal insulators, but suffer from their inability to elongate sufficiently to resist cracking under the pressure of propellant gases. Epoxy, furane, melamine, phenolic, polyester and polyurethane resins are being investigated. Fifteen flexible epoxy resins have been prepared. The flexibilization was accomplished by either chemical modification or physically mixing the commercial resins with plasticizers. The stress-strain properties of the most promising flexible resins will be determined at ambient and at low temperatures.

Mechanism and Prevention of Radiation and Heat Damage in Rubber. Studies are being made to determine the gamma radiation resistance of the various rubbers and the effectiveness of antirads in nitrile rubber. Over 170 potential antirads have been evaluated in a screening program. Three of those evaluated during this period exhibited significant antirad activity. Six fluorine-containing aromatic nitro compounds were included in this investigation to determine whether the strong C-F bond would enhance the antirad activity. The results obtained, based on stress and strain measurement before and after irradiation, indicated that no antirad activity could be attributed to the presence of this particular bond. One of the best antirads discovered for nitrile rubber (1,1'-diphenyl-2-picrylhydrazine) failed to afford any radiation protection to natural rubber. This antirad was also found to be incompatible with the conventional peroxide cure, which is used for dimethyl silicone rubber. The evaluation of different aromatic nitro compounds in nitrile rubber will be continued and the best antirad discovered will be evaluated in natural rubber and in heat-resistant synthetic rubbers. The inhibition of excessive crosslinking in nitrile rubber by the best antirads will also be studied, utilizing a swelling technique, to establish the crosslinking density before and after irradiation.

Other phases of the rubber deterioration program include studies on the effect of various wrappings (Kraft paper, polyethylene, aluminum foil) on long-shelf storage and also bin-life storage program of rubber compounds containing various antiozonants.

Materials for Radiation Shielding. There is also a need for radiation shielding materials. This phase of investigation at Rock Island Arsenal is financially supported by the Ordnance Tank Automotive Command (OTAC), Detroit Arsenal. Two approaches to this problem are to (1) develop high-hydrogen density castable compounds from commercially-available rubbers, and (2) synthesize elastomers containing elements which would permit shielding from high energy neutrons by thermalization and neutron capture.

Thirty-five formulations containing depolymerized natural rubber have been compounded to find room-temperature curing systems. Such accelerators as piperidine-pentamethylene-dithiocarbamate, zinc butyl xanthate activated dithiocarbamate, and p-quinonedioxime have produced satisfactory cures. Test results have shown that this material was not acceptable because the hydrogen density was not sufficiently high for the intended purpose. Butyl rubber has also been depolymerized; however, a room temperature pourable product has not been obtained in sufficient amounts for tests. A promising approach is the reaction of gelling agent, which is formed when a mixture of acrylamide and N.N -methylenebisacrylamide is catalyzed with B-dimethylaminopropionitrile and ammonium persulfate. A stiff gel is formed when this gelling agent is incorporated in a butyl latex (45 percent water) either alone or combined with approximately 10 percent of an emulsifiable polyethylene. This system has high hydrogen density, pourability, and short gelling time. However, it has high moisture absorption from the atmosphere, which is not desirable. The liquid polymer of carboxy-modified polybutadiene has many features desired in a polymer to be used in a castable neutron shield. A great deal of effort has been directed toward finding a suitable room temperature cure for this polymer. Approaches toward finding a curing system can be grouped into four major areas: boron, epoxy, boron-epoxy and the more conventional accelerator-activator type cures. Decaborane and sodium borohydride were found to give a cure, but both were accompanied by severe foaming. On the epoxy-boron formulations, trimethoxyboroxine in combination with epoxy cured the carboxy-modified polybutadiene within six hours. Decaborane with epoxy also gives a good cure. Of the various accelerator-activator type cures, a compound containing tetraethylthiuram disulfide, piperidinium pentamethylenedithiocarbamate, 2-(allylthio) benzothiazole and zinc oxide gave an excellent tack-free cure after 5 days at room temperature. As new materials become available, they will be evaluated for solving the neutron shielding problem. Meanwhile, development shall be continued on those systems showing promise. This shall include efforts to increase hydrogen density, eliminate curing defects (such as foaming) and find optimum curative concentrations.

Another approach to the radiation shielding problem is the preparation of elastomers containing elements which would permit shielding against high energy neutrons by thermalization and neutron capture. Such features would be shown by an organo-boron compound of high molecular weight and high hydrogen density. These elastomers should be easy to process and also be castable. A literature survey has been initiated and is continuing on organo-boron polymers and related boron chemistry. Several methods of synthesis appear suitable to give various end products of the type having: (1) a high molecular weight chain of boron and carbon atoms as the skeleton backbone, (2) a carbon chain skeleton with pendant boron groups or (3) a repeating borate ester chain with boron, carbon, and oxygen in the skeleton.

Selection and Use of Elastomers for Ordnance Applications. Compiling rubber engineering data for the selection and use of elastomers for Ordnance applications is a primary mission of the Rock Island Rubber Laboratory. This is being accomplished by a continuing program of evaluating new elastomers and related materials, and modifying current formulations to produce marked improvement in specific Ordnance items and equipment.

Various attempts were made to improve the properties of vinylidene fluoride/hexafluoropropylene vulcanizates as high temperature by utilizing methods which combine heat plus exposure to gamma rays from a Cobalt-60 source. A water-immersed Cobalt-60 source is shown in figure 2.

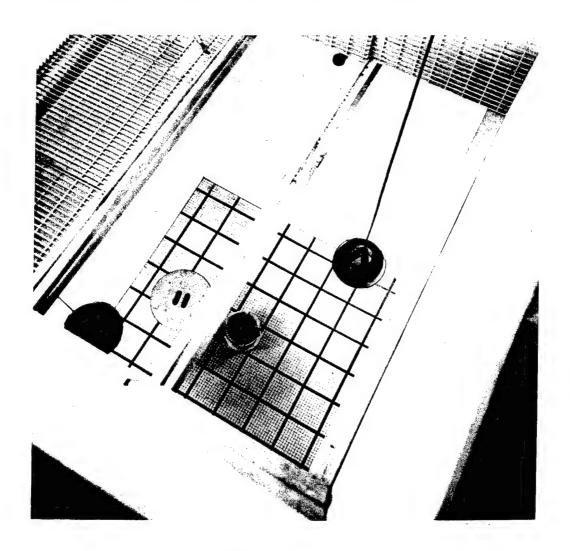


Figure 2

Cobalt-60 Gamma Irradiation Facility at Rock Island Arsenal. Top of well shows sample container in center of ring of Cobalt pencils.

Up to the present time, the following methods for curing vulcanizates have been tried: (1) press cure plus air—oven post cure, (2) press cure plus air—oven post cure plus exposure in Cobalt—60 source, (3) press cure plus exposure to Cobalt—60 source and (4) curing by exposure to Cobalt—60 source. All the vulcanizates cured using any one of the four methods had poor physical properties when measured at high temperatures. Not more than 20 percent of the original tensile strengths of the vulcanizates were retained when tested at  $300^{\circ}$  F.

The outdoor aging of a polyurethane rubber vulcanizates has been completed at Rock Island. Stress-strain and low temperature characteristics were determined after 3, 6, 12, 24 and 36 months outdoor exposure. The deleterious aging effect shown after the first 24 months had increased in rate during the final 12 months as shown by a greater decrease in tensile and modulus values and an increase in percentage elongation. However, approximately 70 percent of its original tensile strength was retained, even after 36 months of outdoor exposure. The identical polyurethane compound, used as control sample, remained unchanged after the first 3 months of shelf-aging.

Two commercially available plasticizers, Admex 515 and Plastolein 9250, have been evaluated in a standard nitrile rubber formulation. Both materials failed to show any advantage over previously tested plasticizers for nitrile compositions. Two other plasticizers for polyurethane rubber were evaluated, but neither showed any improvement on the low temperature flexibility of the compound.

Development and evaluation of new cross-linking agents for rubbers were also undertaken. Twenty-seven curing systems were evaluated using fourteen different polymers. Some of these curing agents produced interesting results. Elemental amorphous boron showed cross-linking reactions with nitrile rubber. Boric oxide cured carboxylic-type elastomers. Dibutyltin sulfide produced 2000 p.s.i. tensile strength with chlorobutyl rubber. Investigation on compounding and vulcanizing various types of rubber for Ordnance applications is a continuing program of the Rock Island Laboratory.

Detroit Arsenal. The rubber research and development program of the Ordnance Corps, conducted at the Ordnance Tank and Automotive Command (OTAC), Detroit Arsenal, Detroit, Michigan, is directed primarily toward improving elastomers for application to Ordnance vehicles and equipment. In addition to its internal laboratory investigations, it establishes and monitors projects to develop more efficient tires, track pads, brake cylinder cups, and other transportation accessories of which rubber is a component part. During the past year, activities at OTAC were concentrated on (1) compounding and evaluation of polyurethane type rubber for track pads and possibly for foam-filled tires, (2) tire and wheel development program, and (3) research studies on protection of rubber items in storage.

Compounding and evaluation of polyurethane type rubber. There is a need for the development of heat-resistant polyurethane compounds that exhibit low-heat build-up properties and excellent water resistance (both as solid and foam compounds) for specific end items, such as track pads, road wheels, and foam-filled tires. Polyurethanes possess excellent tensile strength, abrasion resistance, and other physical properties. If the heat resistance could be increased, it might be possible to use this polymer in many Ordnance applications.

Compounding studies directed toward track pads have developed a polyurethane formulation using 1,4-butane diol as a cross-linking agent which showed significant improvement over the standard. Track pads were made and road tested at Aberdeen Proving Ground over 2,000 miles of gravel, paved, and cross-country roads. The operating temperatures of the track pads were recorded by a hypodermic needle pyrometer. The polyurethane pads operated an average of 25° C. cooler than the standard pads made of Styrene-Butadiene Rubber (SBR). The comparative condition of the track pads are shown in figure 3. Note the difference in chunking resistance of the two rubbers. Although the polyurethane showed more wear than the SBR, the polyurethane has uniform wearability and minimum chunking or chipping; hence, it actually possesses much longer service life than the standard SBR

The highest ambient temperature during this test conducted at Aberdeen, Maryland, was 80° F. Since this test, an improved polyurethane compound (based on laboratory evaluation) has been developed. It has an original tensile strength of 5600 p.s.i. at ordinary room temperature and still retains 1030 p.s.i. at 300° F. Track pads have been made from this compound for tests at Yuma, Arizona, where ambient temperatures are as high as 125°F.

Foam-filled tires were reported last year to have some advantages over air-filled tires. It is now believed that the requirement for heat resistance of a polymer as a foaming material in foam-filled tires is more severe than the track pad requirement. Hence, the actual construction of foam-filled tires is being suspended until a suitable polyurethane compound with outstanding heat resistance is developed. For concept evaluations, the best commercial polyurethane foam compound will be used in fabricating foam-filled tires for exploratory testing.



POLYURETHANE COMPOUND

STANDARD SBR COMPOUND

Figure 3

Illustration of improvement of experimental tank tread pads to wearability and minimum chunking.

Tire and Wheel Development Program. Better tires can be obtained by using improved rubber compounds and proper tire and wheel designs. Road testing is a very essential phase of this development program. Durability tests have been completed on 16-20 Low Profile Tires developed for the medium truck family. Tests indicated that an 8-ply rating tire does not provide satisfactory service for cross-country operation. 10-ply rating Low Profile Tires are now being procured for future tests. Durability and service tests are in progress on storage-aged tires of various sizes to determine comparative service life with new tires. A quantity of tubeless tires and four versions of rims capable of being operated with or without tubes are in operation on the Alcan Highway as a part of a test to evaluate wheel design.

Studies of tread designs to give maximum traction includes screening of rubber compounds made from the rubbers listed below.

Tread - Cis-polyisoprene or oil-extended low-temperature polymer.

Sidewall - Cis-polyisoprene or in combination with Neoprene.

Outer Body and Top Cushion - Natural rubber of Cis-polyisoprene.

Inner Body - Natural rubber of Cis-polyisoprene.

Inner Liner - Halogenated butyl or in combination with natural rubber.

Samples of these compounds, compounded to have maximum weather resistance have been prepared. These samples are undergoing stress-strain, tear, flexing, brittle point, cutability, and accelerated aging tests. In addition, certain drum tests of tires containing some of these compounding features are being conducted to evaluate running temperatures.

A study has been initiated for tank track rubber bushing development from rubber compounds which (1) are sufficiently conductive to dissipate static electrical charge through a 6- by 6- by 1 1/8-inch block, (2) are resistant to ozone and heat aging, (3) meet the -65°F. low temperature brittleness test, and (4) possess an unvulcanized compound which substantially retains its uncured physical and chemical characteristics after 7 days of aging at 158°F., or the equivalent of 6 months of storage under ambient field conditions between 1 April and 1 October at the Red River Arsenal, Texas.

Several compounds had been made from commercially available rubbers. They were processed in conventional laboratory mixing mills and vulcanizing presses, and evaluated in accordance with standards for testing rubber materials established by the American Society for testing Materials. Significant progress has been made. A compound which nearly met all the requirements shall be closely followed and subjected to factory processing. Tests will be conducted on the factory-processed quantity for comparison with those obtained from laboratory-mixed compounds.

Protection of Rubber Items in Storage. Rubber items may be protected against the atmosphere by (1) incorporating antiozonants into the rubber compound before vulcanization and (2) covering the rubber surface with protective films or coatings. Another method of protecting small rubber items in storage is by wrapping them in protective bags such as those made of thin polyethylene film. Packaging antiozonants inside the protective bags will give added protection to the rubber items over extended periods of storage. A project has been initiated to exploit and correct improper methods used for protecting rubber items in storage.

Screening tests (in which rubber loops in holders were inclosed with 5 grams of antiozonant in pint jars, the openings of which were covered with 4-mil polyethylene film punched with six 5.5 millimeter holes) were run on a number of antiozonants. The average ozone concentration inside the box, in which the jars containing the rubber sample were placed, was about 100 parts per hundred million in air. Some of the antiozonants tested have been found to give excellent protection under the conditions of the screening tests. Results obtained thus far have yielded information on the comparative degree of rubber protection provided by various antiozonants. Another phase of this test is the "closed-bag" method which nearly simulates conditions under which packaging antiozonants might be put to practical use. However, this method requires a long time for completion and conclusions drawn from its results are contingent upon the absence of defects in the bag, such as the tightness of the closure.

Exposure tests in which numerous items fabricated with ozoneresistant rubber compounds have been placed at outdoor exposure sites, as well as in the laboratories, are continuing.

# 5. QUARTERMA STER CORPS

In addition to its Army-assigned "research cognizance for elastomers and rubberlike materials", the Quartermaster Research and Engineering Command at Natick, Massachusetts is undertaking an extensive research program to develop new rubbers having those necessary characteristics which are lacking in currently available rubbers. The Command is also doing vulcanizing and compounding development in support of overall Quartermaster Corps projects, including Petroleum, Oil and Lubricant (POL) handling equipment, Thermal Protection, Tentage, Clothing, and Footwear.

- A. Rubber Research. The overall objective of the rubber research is to develop synthetic elastomers possessing a combination of several of the following characteristics: (1) flexibility at extremely low temperatures (-40° F and lower); (2) resistance to attack by chemicals and strong oxidizers, such as aromatic hydrocarbons, strong acids, and other rocket propellants; (3) stability at high temperatures (600° F and higher); (4) flame retardance or non-flammability; (5) radiation resistance; and (6) ozone and weather resistance. The current Quartermaster Corps approaches to the overall objectives are investigations of fluorinated nitroso derivatives, organo-metallic compounds for elastomeric materials, and modified hydrocarbons compounds.
- l. Fluorinated nitroso derivatives. The major portion of the Quartermaster Corps rubber research program is on fluorinated nitroso derivatives. It was reported last year that a nitroso rubber had been synthesized from the copolymerization of trifluoronitrosomethane (CF3 NO) and tetrafluoroethylene (CF2=CF2). The properties of the rubber previously reported (good low-temperature flexibility, unusual chemical resistance, and nonflammability) were based on the evaluation of the unvulcanized materials. During this report period significant progress has been made, both in the methods of polymerization and vulcanization of this rubber. It is believed to be the only known rubber which is nonflammable (See Figure 4).

By improving polymerization methods and techniques, it has been possible to increase the molecular weight of this rubber (as determined by light-scattering techniques) from several hundred thousand to over one million. Correspondingly, the inherent viscosities were increased from 0.3 to 0.8, an improvement which was reflected in the physical and chemical properties of the rubber. Five pounds of this rubber have been sy thesized for vulcanizing and compounding studies.

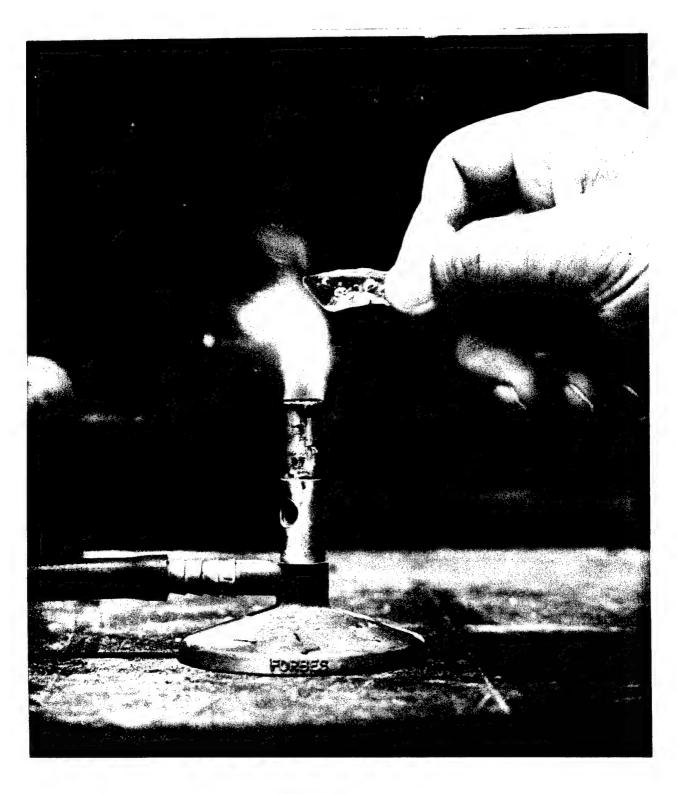


Figure 4

The nitrose rubber is nonflammable when subjected te direct flame

In addition to the CF<sub>3</sub>NO/CF<sub>2</sub>=CF<sub>2</sub> copolymer system, other nitroso derivatives are being explored. Of particular interest are those of ClCF<sub>2</sub>CF<sub>2</sub>NO, NO<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>NO, HCF<sub>2</sub>CF<sub>2</sub>NO and CH<sub>3</sub>CF<sub>2</sub>NO. The monomer HCF<sub>2</sub>CF<sub>2</sub>NO has been prepared from HCF<sub>2</sub>CF<sub>2</sub>Br and copolymerized with CF<sub>2</sub>=CF<sub>2</sub> in an effort to improve tensile properties and response to curatives and reinforcing fillers. The CH<sub>3</sub>CF<sub>2</sub>NO was similarly prepared from the iodides and copolymerized with CF<sub>2</sub>=CF<sub>2</sub>. Work is in progress to develop better and more economical methods of synthesizing nitroso monomers. For example, synthesis of the CF<sub>3</sub>NO by the reaction of CF<sub>3</sub>Br and NO in the presence of ultraviolet light, and with mercury as a catalyst is a slow and expensive process. Some preliminary work has been done on making CF<sub>3</sub>NO by the reaction of trifluoroacetic anhydride and nitrosyl chloride in vacuum. Although the percentage yield is still low, this method is very promising and research will continue toward developing better and less expensive methods for synthesizing nitroso monomers.

Efforts to improve polymerization methods are continuing. An investigation of aqueous suspension and emulsion techniques designed to produce an improved process with more favorable molecular distribution has been initiated.

The progress made on vulcanization studies, using the trifluoronitrosomethane-tetrafluoroethylene copolymer, has been most significant. A
vulcanizing system was developed for this rubber, using a combination of
amines and carbamates as cross-linking agents. Its tensile strength was increased from the 200 pounds per square inch, as reported last year, to the
present strength of 700 pounds per square inch. It was found that a silicon
oxide pigment, HiSil 303, effectively reinforced this rubber, giving it a
tensile strength of 700 p.s.i. and 600 percent ultimate elongation. Investigations on compounding to increase the tensile strength, to develop coating formulations for fabrics, and to exploit the nonflammability characteristics of this new rubber for thermal protective devices and applications
will continue.

The National Aeronautics and Space Administration, the Atomic Energy Commission, and the Army Rocket and Guided Missile Agency have expressed an interest in nitroso rubbers for specialized applications. The Quartermaster Corps is working in close cooperation with these agencies to improve this new material.

2. Organo-metallic compounds for elastomeric materials. Experimental work continued during the past year on the synthesis of organometallic elastomers possessing chemical-resistant and flame-retardant properties. The investigations on organo-tin have been concentrated on copolymers having tin atoms located either in the pendant position or in the backbone of the long chain molecules. Using variations of catalysts and conditions of polymerization, copolymerications have been undertaken with tributyltin methacrylate and the following: bis(chloroethyl) vinyl-phosphonate, hexachlorobutadiene, and chloroprene, with and without small

amounts of methacrylic acid or isoprene. In addition, inorganic acids and alkaline phosphates have been used to provide either acidic or alkaline conditions for copolymerization. In some cases, ferric chloride was added to other catalysts to accelerate the reactions. The tributyltin methacry-late copolymers with fluoro-chloro or phosphorus-vinyl compounds, as well as those from the halogenated dienes, produced materials with insufficient fire-retardant properties. It was found that when ferric chloride was used in a redox-type system, the copolymerization of methacrylic acid and bis(chloroethyl)vinylphosphonate produced a fire-retardant plastic material. So far, attempts to synthesize elastomers possessing fire-retardant characteristics from these materials have not been successful. Continued efforts will be directed toward determining the proper conditions for polymerization reactions.

To produce elastomeric materials with the tin atom in the back-bone of the molecular chain, the reaction of dibutyltin dihydride with monomers such as divinylbenzene, or chloro- and fluoro-dienes has been investigated. In the case of divinylbenzene, a slightly elastomeric material was obtained. The chloro- and fluoro-dienes combined with dibutyltin dihydride to produce plastic products. Investigations have also been directed toward improving vulcanization of a tributyltin methacrylate homopolymer and of a dibutyltin methacrylate-dimethacrylate copolymer. Some degree of improvement resulted but a vulcanizate with higher tensile strength has not yet been obtained. The work on organo-tin is continuing on both the synthesis and polymerization of elastomers and their vulcanization.

The research approach on organo-titanium and organo-zirconium compounds has been similar, that is reacting the metallic compounds with cyclopentadiene to produce ferrocene-type polymers. Attempts to acetylate bis(cyclopentadienyl)titanium dichloride by the Friedel-Crafts reaction were unsuccessful. Reactions were then tried with the two chlorine atoms being replaced by less electro-negative groups such as iodine, phenyl, and p-tolyl. Subsequent acetylation by the same (Friedel-Crafts) reaction yielded the starting material. When 1-bromo-3-chloropropane was reacted with bis(cyclopentadienyl) titanium dichloride and aluminum chloride, the dichloride decomposed. Similar results were obtained by the use of polyhalogenated alkanes. Attempts were also made to cinylate the bis(cyclopentadienyl)titanium dichloride directly with tetravinyltin. A reaction occurred which yielded a yellow-orange powder containing about 25 percent titanium. The powder could not be recrystallized, having apparently decomposed to form a mixture of oxy-titanium compounds. Efforts are now being made to prepare a substituted ferrocene and its subsequent decomposition to a substituted cyclopentadiene which, in turn, should be converted to the desired titanium compound. Further work on organo-titanium will depend on funding factors.

Work on organo-zirconium has been concentrated primarily on vinylation of zircocene dichloride which has been synthesized. Bis (cyclopentadienyl)zirconium dichloride has been monoacetylated as the first step toward formation of a monovinyl zircocene. Attempts to reduce the acetyl compound to alcohol, as the second step, resulted in a breakdown of the compound. Halogenated alkenes and polyhalogenated alkanes were reacted with bis(cyclopentadienyl)zirconium dichloride with no positive results. Currently, work has started on attempting to form a vinyl derivative of cyclopentadiene by acetylating cyclopentadienyl sodium with acetyl chloride, reducing the resulting ketone, and dehydrating the alcohol to form the vinyl compound. The vinyl cyclopentadiene will then be reacted with zirconium tetrachloride to form the vinyl zircocene dichloride.

3. Modified hydrocarbon compounds. During the past year, a small portion of Quartermaster Corps rubber research was directed toward synthesizing modified hydrocarbon monomers such as substituted dienes and olefins to determine whether these materials can produce chemical—and flame—resistant elastomeric materials. A new method of synthesizing a fluoroalkoxy substituted butadiene has been found. This is accomplished by acid catalyzed(H<sub>2</sub>SO<sub>4</sub>) reaction of 3,4-epoxybutene—I with trifluoroethyl alcohol to produce the primary alcohol derivative. This product was then reacted with thionyl chloride (SOCl<sub>2</sub>) in pyridine and subsequently treated with potassium hydroxide (KOH) in an alcoholic solution to form the desired trifluoroethoxybutadiene (CH<sub>2</sub>=CHCOCH<sub>2</sub>CF<sub>3</sub>=CH<sub>2</sub>). This material is currently being investigated as a potential monomer for polymerization into an elastomer.

Polyethers from epichlorohydrin and copolyethers from 2,3-epoxy-butane and epichlorohydrin have been obtained as high molecular weight solids. Gram samples of these polymers have been crosslinked with various dimercaptans and gave elastomeric products. Polythioethers have been prepared both by bulk condensation and by the interfacial polycondensation technique. The latter method gave solid products with the reaction of butadiene dioxide and hexamethylene dimercaptan. Attempts have been made to prepare a number of new dimercaptans for use in the catalytic air oxidation to polysulfides, and also as crosslinking agents for epichlorohydrin polymers and copolymers. Various elastomeric products obtained from this phase of research have been evaluated. Advantages over currently available rubbers and those obtained previously were found to be marginal. For this reason, the work was terminated during August 1960.

B. <u>Vulcanization and Compounding Development</u>. Rubber technologists in the Quartermaster Research and Engineering Command act as consultants on rubber problems for the Quartermaster Corps. The Quartermaster Corps rubber program includes a continuing study on vulcanizing and compounding experimental rubbers so they can be used within the shortest possible lead-time for fabricating rubber items with improved performance. This

phase of investigation includes not only the basic rubbers, but also new compounding ingredients such as antiozonants, plasticizers, accelerators, and reinforcing fillers. For example, there are several new antirads which have been developed during the past few years. One antirad which is effective on nitrile rubber may have no effect on natural rubber as far as resistance to the deteriorating effects of irradiation are concerned.

During the past year, efforts have been directed toward developing rubber compounds which will give improved items in the areas of POL handling equipment, clothing, footwear, and tentage. Work on fluorosilicones has resulted in the development of a gasket compound for quick-connecting gasoline hose that permits coupling of the hose at temperatures as low as minus 50° F. Rubber compounds having a tensile strength of 1400 p.s.i. were made, where previously only 1000 p.s.i. tensile strength was possible. Gaskets made of this new compound were purchased from a commercial source and will undergo engineering tests this year. Within this same area, work is in progress to develop rubber compounds from a nitrile silicone for gasketing material. The nitrile silicone is a new rubber which has excellent low-temperature flexibility and good gasoline resistance, but has poor tensile strength. The best compound developed to date has a tensile strength of 700 p.s.i. A new method of using small amounts of Teflon plastic to improve the strength and tear resistance of the nitrile silicone is being investigated. As this material is considerably less expensive than the fluorosilicone, nitrile silicone gaskets will be made for laboratory testing.

Investigations were also in progress to develop rubber compounds from polyurethanes for use in gasoline hoses and collapsible containers for handling POL products. A polyurethane rubber compound was formulated having improved low-temperature flexibility and high tensile strength but it could not be extruded for making gasoline hose. This investigation is continuing, particularly on extrusion characteristics.

For clothing and footwear applications, several types of rubber are under investigation. A "super" rubber compound using a polyurethane as the basic material has been developed for use in direct molded sole footwear. This new compound will be subjected to a limited engineering test in addition to the usual laboratory evaluation. Realistic and practical specification requirements for direct molded sole footwear will be developed from these tests. Molded boots and dipped gloves made of butyl rubber for protection against toxicological agents are also being investigated. A molded butyl boot was received by this Command through the Canadian Liaison Officer. The boot, manufactured in England, was evaluated for rocket—fuel handlers, protective elething, and toxicological protective clothing. The boot was not recommended for use in rocket—fuel handlers clothing. The Chemical Corps also evaluated this butyl rubber boot and recommended that additional evaluations be made to determine capabilities to protect against toxicological agents. On dipped butyl gloves to

protect against toxicological agents, Quartermaster rubber technologists are giving technical assistance, both on production problems and specification requirements. The Military Clothing and Textile Supply Agency, Philadelphia, Pennsylvania, plans to conduct production tests on the purchase description prepared for this butyl rubber glove.

Development of rubber compounds for use in tentage applications is included in this phase of the program. A silicone rubber-coated shield which is flame-retardant and retains its flexibility at low temperatures has been developed for stovepipe outlets of tents. A purchase description for this item was prepared and successfully production tested.

Compounding and vulcanization studies on a newly-developed rubber, polytrifluorobutadiene, resulted in vulcanizates having a tensile strength of 2800 pounds per square inch. The best vulcanizing agent was found to be dicumyl peroxide. As the overall physical and chemical properties of this rubber were only marginally superior to the commercially available polychloroprene rubber, and because polychloroprene is much less expensive than the polytrifluorobutadiene, no further screening is planned. Another new rubber evaluated during the past year is a copolymer of ethylene and propylene. By hot Banbury mixing with carbon black, vulcanizates having a tensile strength of 3000 p.s.i. were obtained. Dicumyl peroxide was used as a crosslinking agent. This rubber has excellent aging characteristics, but has poor resistance to POL products. Work is continuing on mixtures or blends of this material with other fuel-resistant synthetic rubbers. It is hoped that improved fuel-end ozone-resistant blends can be developed.

Efforts will continue in the area of vulcanizing and compounding developments to assure that the best rubber materials available will be used in Quartermaster Corps supplies and equipment.

The Quartermaster Corps takes advantage of the advice and guidance of the Committee on Elastomers, NAS-NRC Advisory Board on Quartermaster Research and Development. On 17 October 1960, the Committee reviewed the Quartermaster Corps rubber program. The observations and recommendations made by this Advisory Board are presented in Appendix A.

# 6. SIGNAL CORPS

The rubber program of the Signal Corps is conducted at the Signal Corps Research and Development Laboratories, Fort Monmouth, New Jersey.

During the past year, emphasis has been placed on developing polymeric materials with improved dielectric characteristics. In a cooperative project with the University of Pennsylvania, efforts were directed toward preparing and characterizing polyisopropyl acrylate over the entire range of stereo-chemical composition with syndiotactic through atactic to isotactic.

Atactic polymers were prepared by low-conversion, free-radical polymerizations, which were carried out at moderately high temperatures (50° C. to 60° C.). Three fractionations were carried out, yielding about 40 fractions covering a wide range of molecular weights. Syndiotactic polymers were prepared by a free-radical system also, but at lower temperatures (-100° C.) in a Cobalt-60 source. The crystalline polymers obtained were separated by extraction with methanol followed by centrifugation.

Isoactic polymers were obtained from outside sources.

Fractionation of isotactic polyisopropyl acrylate was accomplished by dissolving the polymer in isopropyl alcohol at various temperatures. The fraction (45%) which solubilized at 90°C. is fibrous and has a melting point of 150°C. The second fraction (38%) which dissolved at 59°C. in alcohol is powdery with a melting point of 144°C. The third fraction (17%) which dissolved at 25°C. in alcohol is a rubbery polymer with a melting point of 112°C. The products are being characterized. Due to unavailability of funds, it is planned to discontinue this project, currently funded by Advanced Research Projects Agency.

Polymer degradation studies, conducted in cooperation with the University of Akron, were concentrated on two different polymer systems—biuret—cross—linked poly(ether—urethane) and polysulfide rubber. A theoretical treatment has been developed for the kinetics of recombination of polymer networks during degradation. The results obtained on the two polymer systems were in excellent agreement with experimental data from stress—relaxation measurements. The biuret—crosslinked poly (ether—ure—thane) was found to degrade preferentially at the biuret crosslink, and the efficiency of recombination and the activation energy for scission were both obtained. Also the results on polysulfide rubber were found to be in agreement with known literature values. Degradation studies are expected to be discontinued during the current fiscal year.

The Signal Corps has continuing interest in meteorological balloons for obtaining information on weather conditions at increasingly higher altitudes. The limiting factor is the ability of these balloons to reach the required altitudes due to the degradation of balloon materials by the climatic conditions of the upper atmosphere. For the past several years, efforts have been directed toward developing elastomeric latices which lend themselves to the techniques of fabricating satisfactory meteorological balloons. The approach has been to modify the base material in the rubber latex of polychloroprene from which weather balloons were made. The results showed that modifications made by graft copolymerization with thiols, acrylates, and thioacids gave only marginal improvements. It was also found that the modified materials presented problems in processing by the conventional coagulant-dipping technique. In view of these results, the effort to modify polychloroprene for use in meteorological balloons was discontinued.

Although internal rubber activities have been significantly curtailed, the Signal Corps has continuing problems in electronic and communication applications, particularly on elastomeric jacketing materials for wires and cables. Combinations of such atmospheric influences as ozone, ultraviolet light, oxygen, and extreme temperature, particularly when the elastomer is under stress, produce considerable loss of functional and physical properties of rubber compounds.

The general trend has been to develop and use high density, high molecular weight polyethylene as one-coat extrusions for insulation and jacketing communication wires and cables. These materials have a high resistance to ozone stress cracking. Evaluation of sunproofing waxes for cable jacketing is being investigated. Other activities include characterizing polypropylene, polycarbonate, and polyacetals, and developing procedures for better dispersion uniformity of carbon black in polyethylene.

#### IV FUTURE PLAND

Although much progress has been made by the Technical Services in advancing rubber research and technology during the past several years, much work remains to be done in order to fulfill the specialized rubber requirements needed to support modern military concepts. Future research and development efforts will be directed toward:

#### a. Synthesizing new elastomers

Promising avenues of research have been discovered in the search for new elastomers. These leads will be pursued and possibly increased if FY 1962 levels of funding permit. Emphasis will be placed on the following areas:

- 1. <u>Nitroso derivatives</u>, covering synthesis and polymerization of new monomers to produce elastomers having the best combination of chemical resistance, low-temperature flexibility, nonflammability, and radiation resistance.
- 2. <u>Metasilicate compounds</u>, to develop polymers that remain thermally stable at high temperatures. Results obtained thus far are encouraging.
- 3. Organometallic compounds, including those containing tin, zir-conium, titanium, and other metals, are being investigated as base materials for producing elastomers having high-temperature resistance.
- 4. Organo-inorganic compounds, including boron and nitrogen, to develop materials for radiation shielding. This phase of research has been initiated recently.
- 5. Arylene and fluorine modified hydrocarbons, to determine if aryl structures may impart flexibility at low temperatures to the polymers, and the fluorinated derivatives impart flame resistance.

#### b. Screening evaluation of new elastomers

This phase of investigation is necessary and will continue. Elastomers selected for further investigation require new vulcanization systems. A rubber that cannot be vulcanized does not serve any useful purpose.

# c. Compounding development on experimental and commercial rubbers

Technical Services will undertake compounding development directed toward specific requirements, such as protective masks for the Chemical Corps, tires and track pads for the Ordnance Corps, body prostheses for the Medical Service. This also includes studies on compounding ingredients that go into a rubber formulation, such as antiozonants, antirads, plasticizers, accelerators, vulcanizing agents, and reinforcing fillers.

#### V. COORDINATION WITHIN AND OUTSIDE THE ARMY

In addition to the assigned "primary cognizance for research applicable to the development of elastomers and other rubber-like materials for use in any geographical area", the Secretary of the Army has charged the Quarter-master General with the "responsibility for exchange of pertinent information". Corollary to these assignments, the Quartermaster Corps is maintaining the necessary coordination of the Rubber Research and Development Program both within the Army and with other military agencies. Efficient coordination and exchange of technical information to aviod duplication and unnecessary overlapping of efforts are being maintained through regular meetings and conferences, and by exchange of progress and final reports of both external (contracts) and internal projects.

Within the Army, the Quartermaster Corps initiates an Annual Department of the Army Elastomer Meeting that is held every spring. The last one was sponsored by the Signal Corps and was held at Fort Monmouth, New Jersey. Discussions at this meeting were on an informal basis by working level researchers and technologists. Such informal exchange of ideas has been found to be beneficial in the search for solutions to the numerous problems. Representatives from the Department of Defense and the Army Research Office are always invited to participate. This year's Army Elastomer Meeting is scheduled for 11 - 13 April 1961 at Rock Island Arsenal under the sponsorship of the Ordnance Corps. In addition, meetings between two or more technical services or groups are also held whenever the need arises to discuss and resolve mutual interests and problems. For example, on 15 March 1961, the Quartermaster Corps, the Chemical Corps, and Military Clothing and Textile Supply Agency held a Joint Advisory Industry Committee Meeting on Butyl Rubber Coated Fabrics used in Protective Clothing.

Interservice coordination is also maintained between the Army, Navy, and Air Force. A Joint Army-Navy-Air Force Conference on Elastomer Research and Development is held biennially, the sponsorship of which is rotated between the three Services. The last conference, sponsored by the Army and under the auspices of the Quartermaster Corps, was held in Boston, Massachusetts, on 18 - 20 October 1960. The conference attracted more than 300 leading scientists and researchers in the polymer field. Over 40 technical papers were presented which were grouped into three main categories: (1) basic polymer research, (2) special applications and (3) new elastomers. The agenda for this conference is shown in Appendix B. In addition to the three Military Services, the Department of Defense, National Science Foundation, National Bureau of Standards, and other Governmental agencies participated. There was also considerable international interest in this conference. Representatives from the British Ministry of Aviation and the British Admiralty presented papers concerning rubber research and applications of their respective establishments. The Canadian National Defence Board was also represented. The next Joint Army-Navy-Air Force Conference on Elastomer Research and Development will be held in 1962 under the sponsorship

of the U. S. Department of the Navy. It will probably be held in Washington, D. C. Occasional meetings, as needed, are also held between Services. For instance, on 23 February 1961 a meeting was held at Wright-Patterson Air Force Base, Ohio, between the Quartermaster Corps and the Air Force to discuss and coordinate the research work on fluorine-containing polymers.

Army Technical Services actively participate in national and international meetings and conferences. Significant results obtained from the Department of the Army rubber laboratories are presented (and subsequently published in leading scientific journals) in meetings of the American Chemical Society, American Society for Testing Materials, American Institute of Chemical Engineers, and also in local scientific societies. The Department of the Army participates and has representatives in the International Standardization Organization (ISO/TC45), Technical Committee on Rubber Communications. Exchange of information is being maintained with our counterparts in Canada and the United Kingdom through the Military Liaison Groups of the Tripartite Organization.

APPENDIXES

#### APPENDIX A

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- VULCANIZABLE SATURATED ELASTOMER IN MEDICAL APPLICATION.

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- VULCANIZATION AND PROPERTIES OF TRIFLUORONITROSOMETHANE TETRAFLUORO-ETHYLENE ELASTOMER.
  - J. C. Montermoso, C. B. Griffis, Angus Wilson, and G. H. Crawford, Quartermaster Research and Engineering Command. Presented at National Meeting of the American Chemical Society, New York, New York, September 1960.
- NITROSO-FLUOROCARBON ELASTOMERS.
  - G. H. Crawford, D. E. Rice and J. C. Montermoso, Quartermaster Research and Engineering Command. Presented at Joint Army-Navy-Air Force Conference on Elastomer Research and Development, Boston, Massachusetts, October 1960.
- PROPERTIES OF VULCANIZED NITROSO RUBBER.
  - J. C. Montermoso, C. B. Griffis and Angus Wilson, Quartermaster Research and Engineering Command. Presented at Joint Army-Navy-Air Force Conference on Elastomer Research and Development, Boston, Massachusetts, October 1960.
- STRUCTURE AND PROPERTIES OF NONFLAMMABLE NITROSO RUBBER.
  - J. C. Montermoso, Quartermaster Research and Engineering Command. Presented at National Meeting of the American Institute of Chemical Engineers, Washington, D. C., December 1960.

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Fred Leonard, Army Prosthetics Research Laboratory. Society of Plastic Engineers, Volume 16, No. 9, September 1960.

#### NONFLAMMABLE NITROSO RUBBER.

J. C. Montermoso, Quartermaster Research and Engineering Command. Chemical Engineering Progress, Volume 57, No. 4, April 1961.

### VULCANIZATION AND PROPERTIES OF NITROSO RUBBER.

J. C. Montermoso, C. B. Griffis, Angus Wilson and G. H. Crawford, Quartermaster Research and Engineering Command. Rubber and Plastics Age, Volume 42, No. 5, May 1961

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#### APPENDIX B

NATIONAL ACADEMY OF SCIENCES - NATIONAL RESEARCH COUNCIL ADVISORY BOARD ON QUARTERMASTER RESEARCH AND DEVELOPMENT

# MINUTES OF MEETING 17 OCTOBER 1960

#### COMMITTEE ON ELASTOMERS

### Observations and Recommendations

1. To grasp fully and clearly the progress made in the work on nitroso rubbers since last year, the Committee called for a recapitulation of the accomplishments and for a comparison of the properties of nitroso rubber with those of Buna N and Viton A. The following table was evolved.

Table 1. Nitroso rubber characteristics, progress, and comparison with other chemical-resistant rubbers.

	Progress	
Characteristics	<u>last year</u>	today
Methods of monomer synthesis Monomer yield, %	1 20	4 85
Polymerization Poly molecular weight Polymer intrinsic viscosity	Poor Low 0.15	Very Good Very High 0.80
Vulcanization Reinforcement Tensile strength, p.s.i. Elongation, %	No No 200 500	Yes Yes 700 600

Comparison with other Chemical-Resistant Rubbers

	Nitroso	Buna N	Vitron A
Chemical resistance, Vol. swell, %* Low-temperature flexibility, °C. Flammability ** Ozone resistance	2	24	3
	-40	-13	-13
	No	Yes	Yes
	Excellent	Poor	Good

<sup>\*</sup> Immersion in 30% aromatic fuel for 48 hours at 25°C.

<sup>\*\*</sup> Nitroso rubber will decompose but will not flame when placed in contact with a burning flame. Buna N will burn continuously. Viton A will burn but is self-extinguishing when the ignition flame is removed.

- 2. The members of the Committee made the following observations:
- a. Because of three new techniques for synthesizing monomers, monomers can be made in greater yields and at significantly lower costs than last year.
- b. A very important by-product of the synthesis work is the nitronitrosomethane monomer because of its potential application in the solid propellant field.
- c. Analyses of polymerization methods have led to better polymers. Further studies will delineate optimum conditions for preparing polymers of the best quality.
- d. Nitroso rubber is the first elastomeric material with nitrogen in the backbone that is completely devoid of hydrogen. Such a material might have application in the radiation field.
- e. The Quartermaster Corps is to be highly commended for finding a new unconventional vulcanization process, and especially for finding a unique method of reinforcing this rubber. Most workers would have given up after usual reinforcing agents failed.
- f. Overall, the results from the evaluation of limited quantities of material indicate that nitroso rubber is better than Buna N and Viton A, except in tensile strength. Although a substantial improvement in tensile strength has been realized during the year. it is firmly believed that compounding studies will increase it further. The expected low-temperature characteristics of nitroso rubber have been confirmed. Its chemical resistance is excellent. It does not flame the gases evolved from the decomposition might be sufficient to blow out the flame source.
- 3. Closely coupled with any research and development project is the profitable use of the end item. A partial listing of the possible military and civilian applications of nitroso rubber includes:

#### Military

- l. Fabric coating for use in uniforms, ponchos, etc.
- 2. Rubber components in flame—throwing apparatus.
- 3. Gaskets, hoses, and seals exposed to chemicals under Arctic operations.

#### Civilian

- l. Fire fighters suits.
- 2. Hoses and gaskets, etc.
- 3. Civil Defense protective items.
- 4. Potential use in National Aeronautics and Space Commission and Atomic Energy Commission applications, such as propellant binders and explosives.

7 4

- 4. In view of the appreciable progress made during the past year and because of the advantages and potential applications of nitroso rubber summarized in a. and b. above, the members of the Committee sincerely regret that adequate funds are not available for a more rigorous effort to accelerate a substantial breakthrough. Citing the serious need for more investigative work on monomers and polymers, and the growing need for compounding studies on a broader basis than heretofore, the Committee strongly recommends that a vigorous effort be made to acquire additional support for this particularly promising program.
- 5. From their own experiences, the members of the Committee know that large amounts of material are necessary for a comprehensive compounding study. The Committee accordingly recommends that the Quartermaster Corps look into the cost of 100, 500, and 1,000 lbs. of nitroso rubber for the purpose of purchasing an appropriate amount for extensive compounding research during the next year.
- 6. To capitalize on the progress made thus far, and to prevent spreading the effort too thin with a limited budget, the Committee recommends that for the present time the program place emphasis on methyl and ethyl nitroso rubbers.
- 7. In addition to the effort on nitroso rubbers, the members of the Committee unanimously agree that a continuing external and internal program on new monomers and polymers should be maintained. This continuing type of exploratory work is necessary to provide future elastomer developments to fulfill the specific military operational requirements.

#### Committee Members

Dr. R. F. Dunbrook Mr. C. H. Alexander

Dr. W. B. Reynolds

Mr. H. F. Robertson

Dr. Loren B. Sebrell

Dr. Lawrence A. Wood

- Firestone Tire & Rubber Company

- B. F. Goodrich Chemical Company

- General Mills, Inc.

- Union Carbide Corporation

- International Latex Corporation

Dr. Warren S. Stubblebine - Stowe-Woodward Company, Inc.

- National Bureau of Standards

#### APPENDIX C

#### **AGENDA**

JOINT ARMY-NAVY-AIR FORCE CONFERENCE ON ELASTOMER RESEARCH AND DEVELOPMENT Boston, Massachusetts 18 - 20 October 1960

General Chairman: Dr. J. C. Montermoso, QMR&E Command

18 October 1960

SESSION I - OPENING REMARKS & INVITED PROGRAM STATEMENTS

OPENING REMARKS

Dr. G. R. Thomas, Chief, Chemicals & Plastics Div., QMR&E Command

INTRODUCTION

Brig. General Merrill L. Tribe, Commanding General, QMR&E Command

WELCOME ADDRESS

Major General Roy T. Evans, Jr., Deputy The Quartermaster General

THE HOLE IN THE FABRIC OF RESEARCH

J. R. Townsend, Special Assistant to Director of Defense, R & E

SUPPORT OF BASIC RESEARCH ON HIGH POLYMERS Alex Kotch, National Science Foundation

SOME U. K. DEVELOPMENTS IN THE ELASTOMER FIELD

H. Warburton Hall and W. H. Edwards, Ministry of Aviation,
United Kingdom

THE ORGANIZATION AND STATUS OF ELASTOMER RESEARCH IN THE BRITISH ADMIRALTY

G. N. S. Farrand, Admiralty Materials Laboratory, United Kingdom

HIGHLIGHTS OF EUROPEAN POLYMER RESEARCH

J. H. Faull, Jr., Office of Naval Research

JOINT ARMY-NAVY-AIR FORCE CONFERENCE ON ELASTOMER RESEARCH AND DEVELOPMENT Boston, Massachusetts

#### 18 October 1960

#### SESSION II - BASIC POLYMER RESEARCH

Chairman: J. M. Kelble, Wright Air Development Division

CHAIN ENTANGLEMENTS & MECHANICAL PROPERTIES OF AMORPHOUS POLYMERIC SYSTEMS

T. G. Fox. Mellon Institute

CHAIN DIMENSIONS OF POLYMERIC CHAINS
C. A. J. Hoeve, Mellon Institute

ROLE OF ENTANGLEMENTS IN DEGRADATION OF ELASTIC NETWORKS

K. W. Scott, V. R. Allen, and M. Morton, University of Akron

POLYMER STRUCTURE AND ITS RESISTANCE TO A CHEMICAL AGENT K. C. Tsou and B. D. Halpern, Borden Chemical Company

ANTIOXIDANT ACTION IN POLYMERS

F. H. Winslow, W. L. Hawkins, and M. A. C. Worthington, Bell
Telephone Labs, Inc.

ZONE REFINING FRACTIONATION OF POLYMERS

J. D. Loconti, QMR&E Command and J. W. Cahill, Lord Mfg. Company

MECHANISM OF AMINE CROSSLINKING OF FLUOROELASTOMERS K. L. Paciorek, Wyandotte Chemical Corporation

AROMATIC FLUOROCARBONS: THERMAL STABILITY AND SYNTHESIS L. A. Wall, National Bureau of Standards

POLYAROMATICS

J. E. Mulvaney, H. Vogel, T. Otsu, C. B. Abshire, M. Hasegawa, and C. S. Marvel, University of Illinois

SYNTHESIS OF ORGANO-LEAD POLYMERS RELATED IN MOLECULAR STRUCTURE TO SILICONE ELASTOMERS

A. D. Delman, B. B. Simms, E. Klein, and J. Mironov, New York Naval Shipyard

JOINT ARMY-NAVY-AIR FORCE CONFERENCE ON ELASTOMER RESEARCH AND DEVELOPMENT Boston, Massachusetts

#### 19 October 1960

#### SESSION II - BASIC POLYMER RESEARCH (Continued)

- SILICON-NITROGEN POLYMERS AND THEIR COORDINATION E. G. Rochow, Harvard University
- INORGANIC POLYMERS CONTAINING COORDINATED SPECIES

  B. P. Block and <u>G. Barth-Wehrenalp</u>, Pannsalt Chemicals Corp.
- THERMALLY—STABLE METALLIC SALTS OF POLYVINYLPHTHALIC ACID

  E. C. Winslow and A. Laferriere, University of Rhode Island
- POLY(TRIORGANOMETALLOXY) AND POLY(CHELATED) METALLOXANE POLYMERS

  J. B. Rust, C. L. Segal, and H. H. Takimoto, Hughes Aircraft

  Company
- POLYMER PROGRAM AT WRIGHT AIR DEVELOPMENT DIVISION
  W. Gibbs, Wright Air Development Division, U. S. Air Force

#### SESSION III - SPECIAL APPLICATIONS

Chairman: Dr. J. H. Faull, Jr., Office of Naval Research

- EFFECT ON ELASTOMERS OF EXPOSURE AT TEMPERATURES UP TO 1000° F.

  L. J. Kitchen, G. L. Hall, and J. D. Rigby, Firestone Tire & Rubber Company
- SEALANTS FOR ADVANCED FLIGHT SYSTEMS
  P. A. House, Wright Air Development Division, U. S. Air Force
- A HIGH-TEMPERATURE PROTECTIVE SYSTEM FOR CROSS-LINKED POLYETHYLENE C. I. Carr and R. Miller, U. S. Rubber Company
- NEW MONOMERS FOR POTENTIAL RADIATION—RESISTANT POLYMERS W. L. Beears and R. J. Fawcett, B. F. Goodrich Company
- EFFECT OF AMINE ADDITIVES ON COMPRESSION SET, CROSS-LINKING AND CHAIN SCISSION IN AN IRRADIATED RUBBER VULCANIZATE

  W. E. Shelberg, J. F. Pestaner and L. H. Gevantman, U. S. Naval

Radiological Defense Laboratory

# JOINT ARMY-NAVY-AIR FORCE CONFERENCE ON ELASTOMER RESEARCH AND DEVELOPMENT

# Boston, Massachusetts

#### 19 October 1960

# SESSION III - SPECIAL APPLICATIONS (Continued)

MECHANISM OF IONIZING RADIATION DAMAGE OF SBR ELASTOMERS

A. D. Delman, I. J. Stanley, B. B. Simms, A. E. Ruff, and
E. Goldberg, New York Naval Shipyard

ELASTOMERS FOR CRYOGENIC SEALING

F. W. Tipton, G. E. Trepus, and R. S. Roper, Boeing Airplane Co; and D. H. Weitzel, and R. F. Robbins, Cryogenic Engineering Lab., National Bureau of Standards

POLYMER COMPATIBILITY IN ROCKET FUELS AND OXIDIZERS

J. Green and N. Levine, Reaction Motors Division, Thiokol Chemical
Corporation

RHEOLOGICAL AND SPRAY PROPERTIES OF DILUTE POLYMER SOLUTIONS L. Cohen and G. W. Rodon, Army Chemical Center

RUBBER MATERIALS FOR DAMPING VIBRATION OF METAL STRUCTURES R. E. Morris, Mare Island Naval Shipyard

VISCO-ELASTIC DAMPING MATERIALS
D. H. Kallas, New York Naval Shipyard

COMPOSITE SEAL MATERIALS

M. Sabanas and F. Iwatsuki, Armour Research Institute

TRANSIENT PROPERTIES OF THREE CASTABLE POLYURETHANE COMPOUNDS W. B. Lew and W. Sergeant, Puget Sound Naval Shipyard

FOAMED-RESILIENT MATERIALS AND RUBBERIZED-HAIR FOR PACKAGE CUSHIONING APPLICATIONS

S. A. Eller, A. A. Stein, and C. K. Chatten, New York Naval Shipyard

POLARIS STOWAGE-AND-LAUNCE ADAPTERS
R. E. Morris, Mare Island Naval Shipyard

JOINT ARMY-NAVY-AIR FORCE CONFERENCE ON ELASTOMER RESEARCH AND DEVELOPMENT Boston, Massachusetts

19 October 1960

SESSION III - SPECIAL APPLICATIONS (Continued)

COMPOUNDING FOR PROTECTIVE MASKS

H. H. Anderson, General Tire & Rubber Company

VULCANIZABLE SATURATED ELASTOMERS IN MEDICAL APPLICATION F. Leonard, Army Prosthetics Research Laboratory

Statler-Hilton Hotel, Boston, Massachusetts

Guest Speaker - Dr. Richard A. Weiss, Deputy and Scientific Director, Army Research Office, OCRD, Department of the Army, Washington, D. C.

Subject - BY SCIENCE, FOR TECHNOLOGY

20 October 1960

SESSION IV - NEW ELASTOMERS

Chairman: Dr. R. F. Dunbrook, NRC Advisory Board on QMR&D

LOW-TEMPERATURE POLYESTER ELASTOMERS

A. W. Sloan, W. D. Stewart, and J. Terek, Atlantic Research Corp.

EVALUATION OF CYANOPROPYL SILICONE ELASTOMERS

D. B. Braun and E. W. Bennett, Union Carbide Corporation

SYNTHESIS OF ARYLENE-MODIFIED SILOXANES

G. M. Omietanski and W. G. Reid, Union Carbide Corporation

HEAT-AND RADIATION-RESISTANT ARYLENE-MODIFIED SILOXANES

Z. T. Ossefort, Rock Island Arsenal

ELASTOMER RESEARCH AT WRIGHT AIR DEVELOPMENT DIVISION

W. R. Griffin, Wright Air Development Division

JOINT ARMY-NAVY-AIR FORCE CONFERENCE ON ELASTOMER RESEARCH AND DEVELOPMENT Boston, Massachusetts

20 October 1960

### SESSION IV - NEW ELASTOMERS (Continued)

THE SYNTHESIS OF FLUORINE-CONTAINING MONOMERS P. Tarrant, University of Florida

SYNTHESIS OF FLUORINATED NITROSO MONOMERS

A. P. Stefani, J. R. Lacher, and J. D. Park, University of Colorado

NITROSO-FLUOROCARBON ELASTOMERS

G. H. Crawford, D. E. Rice, Minnesota Mining & Mfg. Co., and J. C. Montermoso, Quartermaster Research & Engineering Command

PROPERTIES OF VULCANIZED NITROSO RUBBER

J. C. Montermoso, C. B. Griffis, and Angus Wilson, Quartermaster
Research & Engineering Command

Concluding Remarks: W. G. Parks, National Research Council

ADJOURNMENT

### APPENDIX D

# TECHNICAL SERVICES PROJECTS WITHIN THE DEPARTMENT OF ARMY ELASTOMER RESEARCH & DEVELOPMENT PROGRAM

### CHEMICAL CORPS

# External Projects

		Amount	
Contractor and Contract No.	Project Description	FY 1961	Plans for FY 1962
Borden Chemical Co. DA18-108-405-CMI-297	Polymeric materials for Chemical Corps Use	<b>\$7</b> 5, <b>00</b> 0	
General Tire & Rubber Co. DA30-070-CML-916	Compounding Study for Protective Masks	\$14,000	\$40,000
Franklin Institute DA-18-108-CML-75	Break⇒up of Viscoelastic Fluids	\$20,000	200 (CC) (CC) (CC) (CC) (CC) (CC) (CC) (C
	TOTAL	\$109,000	\$40,000
	Internal Projects		
	COMMITTED CANCEL COMPANY AND	An	ount
Project No.	Project Description	FY 1961	Plans for FY 1962
904-2316-4321	Field Protective Mask Rubber Component Testing, Evaluation and Assembly	\$10,000	\$10,000
4 <b>C</b> =08=03=016=10	Physico-Chemical Agents	\$20,000	\$20,000
, 4375 <sub>A</sub> 24	TOTAL	\$30,000	\$30,000

### CORPS OF ENGINEERS

# Internal Projects

Project No.		Amount	
	Project Description	FY 1961	Plans for FY 1962
8593-31-001-04	Application of Rubber to Engineer Equipment	\$30,000	\$25,000
8 <b>5</b> 93-31-001-05	Coated Fabric for Engineer Applications	\$ 5,000	\$10,000
	TOTAL	\$35,000	\$35,000

### MEDICAL SERVICE

Project No.		Amount	
	Project Description	FY 1961	Plans for FY 1962
S-49-024	Elastomer Problems	\$40,000	\$50,000
	TOTAL	\$40,000	\$50,000

#### ORDNANCE CORPS

#### Rock Island Arsenal

# Rubber Program at Rock Island is funded and directed by Ordnance Material's Research Office, Watertown Arsenal

# External Projects

		A	mount
Contractor and			Plans for
Contract No.	Project Description	FY 1961	FY 1962
Resin Research Lab	Heat Resistant Inhibitors	\$ 28,000	\$ 28,000
DA-11-070-508-ORD-1200	for Diene Rubber	•	
Atlantic Research Corp.	Flexible Polymers for In-	\$ 50,000	\$ 50,000
DA-36-034-ORD-3325-RD	sulation in Rocket Motors		
Stanford Research Inst.	Specialty Silicone Elas-	\$ 37,000	
DA-11-070-508-ORD-906	tomers		
Aerojet-General Corp.	Modified Metasilicates	\$ 40,000	\$ 40,000
DA-04-495-ORD-3075	for High Temperature Use		
Hughes Aircraft Co.	Rocket Liner Materials	\$100,000	\$100,000
DA-04-495-ORD-3079	(Semi-inorganic Polymers)		
Yarsley Res. Lab	Novel Silicone-Based Mono-	\$ 14,000	\$ 14,000
DA-91-591-EUC-1445	mers and Polymers		
	TOTAL	\$269,000	\$232,000

		Amount	
			Plans for
Project No.	Project Description	FY 1961	FY 1962
OMS Code	Ordnance Structural Poly-	\$100,000	\$100,000
5010-11-8060051	meric materials		
OMS Code	Materials for High Tempera-	\$ 22,000	\$ 60,000
5010-11-8080051	ture Use		
OMS Code	Materials for Radiation	\$ 50,000	
5510-12-28500-01-03	Shielding	Funded by	
		OTAC	
	TOTAL	\$172,000	\$160,000

#### ORDNANCE CORPS

# External Projects (For Tank and Automotive Applications, Ordnance Tank and Automotive Command, Detroit Arsenal)

		A	mount
Contractor and Contract No.	Project Description	FY 1961	Plans for FY 1962
Dayton Rubber Co. DA-33-008-ORD-1799	Urethane Elastomers with Low Hysteresis & Heat Stability	\$21,000	\$30,000
U. S. Rubber Co. DA-20-018-ORD-23031	Goer Tires - Radical Ply	\$98,500	සර යා සා මිට මිට වේ සිට
U. S. Rubber Co. DA-20-018-ORD-20440	Tires for New Family of Medium Tactical Truck	\$43,000	\$43,000
Firestone Tire & Rubber Co. DA-33-019-ORD-3478	Goer Tires	\$97,000	<u></u>
U. S. Rubber Co. DA-20-018-ORD-23117	Puncture-Resistant Tires	\$12,000	<b>⊕</b> ₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩₩
J. W. Haagen∞Smit DA-04-495-ORD-1969	Exposure Testing of Rubber Component	\$ 4,000	\$ 2,000
Burke Research Co. DA-20-018-0RD-22837	Antiozonants for Rubber Protection in Storage	\$15,000	
U. S. Rubber Co. DA-11-022-ORD-3375	Improved Vulcanizates for Use in Tank tracks, road-wheels, etc.	\$50 <sub>0</sub> 000	\$49,000
U. S. Rubber Co. DA-20-089-ORD-39182	Cis-polyisoprene for Re- tread Materials	\$ 4,500	######################################
Baldwin Rubber Co. DA-20-089-ORD-39183	Polychloroprene Retread Materials	\$ 6,000	ලාතු <b>සා</b> යාදා සා සා
	TOTAL	\$351,000	\$124,000

#### ORDNANCE CORPS

# External Projects (For Tank and Automotive Applications, Ordnance Tank and Automotive Command, Detroit Arsenal)

		Amount	
Contractor and Contract No.	Project Description	FY 1961	Plans for FY 1962
Firestone Tire & Rubber Co. DA-33-019-ORD-3322	Ozone Resistant and Electrically Conductive Rubber	\$ 2,500	
U. S. Rubber Co. In process of Ne- gotiation	Butyl Rubber for Retread Materials	\$ 4,500	accopswapted
	TOTAL	\$ 7,000	

Project No.		Amount	
	Project Description	FY 1961	Plans for FY 1962
OMS - Code No. 5510-12-25500	Vehicle Testing (Rubber Compounds)	\$149,000	
OMS - Code No. 5510-12-25500	Rubber Items, Vehicles Components & Accessories	\$ 73,000	\$11,000
OMS - Code No. 5510-12-21700	Polyurethane Foam∞filled Tires	\$ 13,800	\$10,000
	TOTAL	\$235,800	\$21,000

# QUARTERMASTER CORPS

### External Projects

		Amount	
Contractor and Contract No.	Project Description	FY 1961	Plans for FY 1962
Minnesota Mining & Mfg. Co. DA-19-129-QM-1684	Chemical-Resistant Fluoro- ines containing Rubbers	\$65,000	\$80,000
Univ. of Florida DA-19-129-QM-500	Synthesis of Fluorocarbon Monomers	\$26,000	\$26,000
Univ. of Colorado DA-19-129-QM-1263	Synthesis of Fluorinated Nitroso Compounds	\$24,000	\$26,000
Univ. of Buffalo DA-19-129-QM-1271	Semi-organic Chemical - Resistant Elastomers	Expires Jan. 1961	To be dis- continued
U. S. Rubber Co. DA-19-129-QM-1696	Development of Rubber Stocks for POL Handling Equipment	\$13,500	To be discontinued
Hodgman Rubber Co. DA-19-129-QM-1220	Development of Coated Fab- rics	Expired 31 Dec 60 \$128,500	\$132,000

			ount
Project No.	Project Description	FY 1961	Plans for FY 1962
7-93-15-004	Rubber Research	\$82 <u>,000</u>	\$82,000
<b>7</b> -53-03-024B	Elastomers for POL Handling Equipment	\$ 5,600	
7-93-30-001	Coated Fabrics TOTAL	\$37,000 \$124,600	\$82,000

### SIGNAL CORPS

# External Projects

Contractor and Contract No.		Amount	
	Project Description	FY 1961	Plans for FY 1962
Univ. of Akron DA-36-039-SC-74982	Degradation Studies on Condensation Polymers	\$40,000	
Princeton Univ. DA-36-039-SC-78105	Polymers for Electronic Applications	\$40,000	\$40,000
	TOTAL	\$80,000	\$40,000

Project No.	Project Description	Amount	
		FY 1961	Plans for FY 1962
3G93-34-001-03-01	Reinforced Organic Thin Films	\$20,000	\$20,000
3A99-15-001-01-13	Electronically Functional Organic Materials	\$25,000	\$25,000
	TOTAL	\$45,000	\$45,000

### DISTRIBUTION

Chief Chemical Officer

Chief of Engineers

Chief of Ordnance

Chief Signal Officer

Chief of Transportation

Office of Naval Research (Bureau of Supplies and Accounts)

Air Research & Development Command

Commandant, Army War College at

Carlisle Barracks, Pa. ATTN: Library

U. S. Marine Corps